# CHARACTERIZATION OF A RESINITE MACERAL FRACTION

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## INTRODUCTION

Resinite in coals is attributed to plant resins and essential oils in leaves which are converted during coalification to spherical or oval shaped bodies and occasionally lenses or thin bands of fluorescing material (1). Chemically, the resins consist of terpenoid structures (2). Resinite is often found in Tertiary brown coals and is even found in Carboniferous bituminous coals (1). Reflectance, refractive index, fluorescence wavelength and other optical properties vary with origin of the resins and the degree of maturation. The observation of resinites in cell fillings indicates that at some point in the coalification process, the resinite is relatively fluid. In the Lower Cretaceous period, conifers were a source of resins for incorporation into coal. In the Upper Cretaceous period, angiosperms which are richer in waxes began to appear and coals of this period would contain relatively more wax and less resinite.

In a study of the swelling of coal macerals in organic solvents, a resinite maceral fraction was separated from Hiawatha, Utah coal. Hiawatha coal is from the Wasatch Plateau field, and dates from the Cretaceous period. Coals of the Wasatch Plateau are relatively rich in resinite. As part of the study of maceral swelling, the properties of the resinite fraction were measured.

## EXPERIMENTAL

Maceral fractions were prepared by density gradient centrifugation according to the method of Dyrkacz and Horwitz (3). The coal was ground in a ball mill and then in a fluid energy mill until the size was reduced to less than 10 microns. The sample was demineralized with HCl and HF and introduced into the density gradient prepared from aqueous CsCl. After centrifugation, the gradient was displaced by a heavy fluid and fractions of different density were collected in a fraction collector. A sample obtained by commercial flotation of larger resinite particles was also used in this study.

Solubilities were measured in organic solvents in Soxhlet extractors at the boiling point of the solvent. Swelling of the whole coal samples was measured by the method of Green et al. (4). Coal was centrifuged, solvent added and allowed to come to equilibrium and the sample was again centrifuged. The increase in the height of the column of coal was used as a measure of swelling.

## RESULTS AND DISCUSSION

Properties of Hiawatha coal and the resinite fraction separated from Hiawatha coal are listed in table 1. The coal is a high volatile bituminous B coal. Resin particles are visible in the raw coal lumps. Petrographic analysis indicates that resinite comprises 11 percent of the coal. The density distribution of the Hiawatha coal is shown in figure 1. The resinite fraction does not show as a distinct peak, although the material with a density less that 1.10 g/cm$^3$ represents about 11% of the total sample and has the appearance and properties of resinite. The density distribution of a resinite sample obtained by flotation is also shown in figure 1. The sample shows a narrow density distribution of 1.01 to 1.06 g/cm$^3$ and an average density of about 1.04 g/cm$^3$. This differs significantly from the vitrinite density of about 1.28 g/cm$^3$ for Hiawatha coal and exinite densities of 1.16 g/cm$^3$ for bituminite and 1.19 g/cm$^3$ for sporinite measured in other coals.

Hiawatha coal shows the typical swelling behavior of bituminous coals. Maximum swelling was observed in pyridine and a bimodal curve was obtained when swelling was plotted versus solubility parameter. The second maximum in THF at a solubility parameter of about 19 MPa$^{1/2}$ is attributed to solvation of the macromolecular structure of the coal with an increase in hydrodynamic volume while the swelling in pyridine is associated with cleavage of hydrogen bonds which serve as crosslinks and limit coal swelling (5). The resinite fraction shows a high solubility in solvents with solubility parameters in the range 15 to 20 MPa$^{1/2}$. The solubility is shown if figure 2. Solubility is high in non-polar and moderately polar solvents, but is very low in pyridine or methanol. Although the resinite comprises 11% of the whole coal sample, solubility of the coal in the non-polar solvents is less than 11%.

Murchison (6) studied a group of hand-picked resinite samples. Samples from bituminous coals showed carbon contents of the range observed for the Hiawatha resinite, but hydrogen contents were significantly less, 7-9% compared to 12%. The hydrogen to carbon ratios were 1.04 to 1.35 compared to 1.72 for the Hiawatha resinite. Oxygen contents were about double that observed in the Hiawatha resinite. Infrared spectra of the resinite fraction shows strong absorption due to aliphatic C-H species in the range 2800-3000 cm$^{-1}$. Sharp bands are observed at 1370 and 1450 cm$^{-1}$, attributed to aliphatic structures. Only slight absorption is observed from the O-H group at 3300 cm$^{-1}$. A broad absorption occurs at 1600 cm$^{-1}$ and more intense absorption at 1700 - 1750 cm$^{-1}$. Broad absorption also occurs at 1000-1200 cm$^{-1}$. The spectra is in agreement with the high hydrogen content which indicates an aliphatic structure.

Thermal gravimetric analysis shows weight loss starting at 275C and a maximum rate of weight loss at 440C. The weight loss to 700$^{\circ}$C was 86%, less than the observed volatile matter content. Pyrolysis of the whole coal samples shows loss of the fluorescing resinite after heating to the range 400 to 450C in nitrogen (7). Heating in hydrogen decreases the temperature at which the resinite fluorescence disappears.

## CONCLUSIONS

Relatively pure resinite fractions can be recovered from coal using the density gradient centrifugation technique. The resinite separated from Hiawatha, Utah coal is highly aliphatic. The chemical structure of this resinite appears to be different from those of amber and resinites from bituminous coals and lignites separated and studied by Murchison (6), although some of the differences may be attributed to purity of the samples. The unique properties of the resinite account for its use as a chemical.

## ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, contract number DE-FG22-84PC70796.

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Table 1. Properties of Hiawatha Coal
and Resinite Maceral Fraction

| | Hiawatha Coal | Resinite Fraction |
|---|---|---|
| Carbon, maf % | 77.6 | 83.7 |
| Hydrogen, maf % | 6.4 | 12.0 |
| Nitrogen, maf % | 1.4 | 0.4 |
| Sulfur, maf % | 1.2 | |
| Oxygen, % (difference) | 13.4 | 3.9 |
| H/C, atomic ratio | 0.99 | 1.72 |
| Moisture, % | 1.6 | 0.3 |
| Ash, % | 19.4 | 0.5 |
| Volatile Matter, % | 36.5 | 93.9 |
| Heating Value, Btu/lb | 13,917 | 18,095 |
| Vitrinite Reflectance, % | 0.48 | |
| Petrographic Analysis | | |
| Vitrinite, % | 75.7 | |
| Semifusinite, % | 4.0 | |
| Fusinite, % | 0.7 | |
| Macrinite, % | 6.2 | |
| Sporinite, % | 0.6 | |
| Resinite, % | 11.0 | |
| Cutinite, % | 1.8 | |

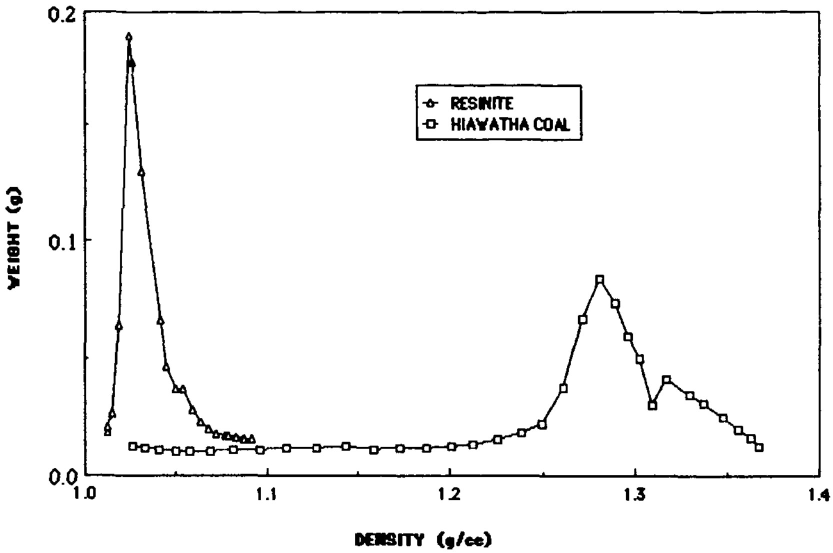

Figure 1. Hiawatha Coal and Resinite Maceral Density

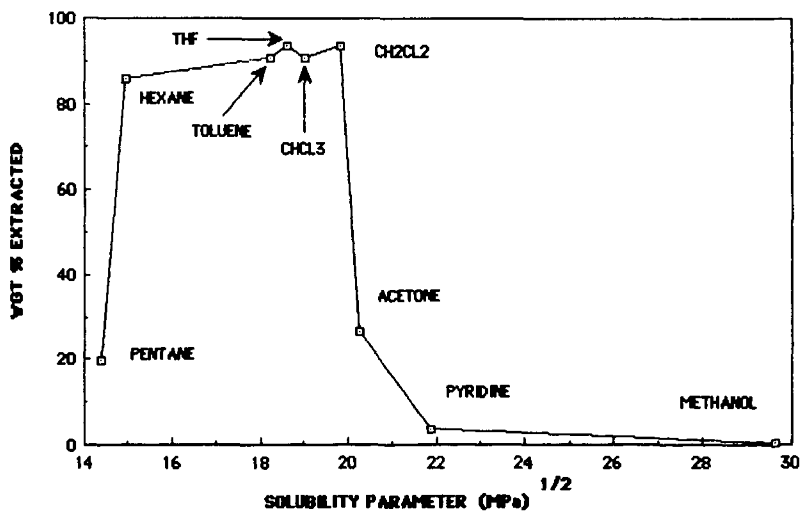

Figure 2. Solubility as a function of Solubility Parameter